BENZENE AS AN INDOOR AIR POLLUTANT IN FAIRBANKS, ALASKA

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ABSTRACT

Benzene is a known carcinogen found in gasoline, automobile exhaust, cigarette smoke, and organic solvents. Previous studies suggest that sources of chemicals within the home are the major factors influencing personal exposure to benzene. Indoor air was sampled for benzene in order to determine the concentrations present in Fairbanks homes, and to identify what factors might be associated with higher concentrations. Sampling sites were limited to homes with attached garages and with no smokers in the household.

A wide range of benzene concentrations was observed in the eight homes sampled. The highest concentration was about 70 ppbv, and the concentration in most homes was at or above 4 ppbv. The primary source of benzene appears to be gasoline, most likely from small engines (such as lawnmowers) stored in the attached garage. More sites, including homes with attached garages that contain various numbers of small engines, need to be sampled to confirm these conclusions.

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ACRONYMS AND ABBREVIATIONS

ACGIH	American Conference of Governmental Industrial Hygienists
ADEC	Alaska Department of Environmental Conservation
EPA	Environmental Protection Agency
GC	gas chromatograph
GC-FID	gas chromatograph equipped with a flame ionization detector
GC-MS	gas chromatograph equipped with a mass spectrometer
MTBE	methyl tertiary butyl ether
NIOSH	National Institute for Occupational Safety and Health
OSHA	Occupational Safety and Health Agency
PC	personal computer
PEL	Permissible Exposure Limit
ppb (ppbv)	parts per billion (by volume)
ppm (ppmv)	parts per million (by volume)
REL	Recommended Exposure Limit
SLPM	standard liters per minute
STEL	Short Term Exposure Limit
TLV	Threshold Limit Value
TWA	Time Weighted Average

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Chapter 1

INTRODUCTION

In northern locations, where people spend a great deal of time indoors during the winter, indoor air quality is especially important. One potential source of indoor air pollution is benzene, a known carcinogen. Long-term exposure to relatively low levels of benzene is associated with leukemia and other diseases of blood-forming tissue, as well as other types of cancer (Goldstein et al, 1992). Potential sources of benzene include gasoline, automobile exhaust, cigarette smoke, solvents, paints, stains, and glues (Goldstein et al, 1992).

Exposure limits for benzene have been established for workplace environments. The Occupational Safety and Health Agency (OSHA) standards are described as Permissible Exposure Limits (PEL's), the American Conference of Governmental Industrial Hygienists (ACGIH) sets Threshold Limit Values (TLV's), and the National Institute for Occupational Safety and Health (NIOSH) establishes Recommended Exposure Limits (REL's). Whatever term is used for the standards, there are generally three categories. The Time Weighted Average (TWA) limit describes the average concentration, over a normal workday (usually 8 hours) and work week (40 hours), to which most workers can be exposed repeatedly without adverse effects. The Short Term Exposure Limit (STEL) describes the concentration to which workers can be exposed for short periods of time (usually 15 minutes) without serious effects, and should not be exceeded at any time during the workday, even if the TWA exposure remains within the

recommended limit. The ceiling limit is the concentration that should not be exceeded for any amount of time during the workday (3M Company, 1996). The TWA limit is most relevant when considering the types of chronic exposure that would occur in residential settings.

OSHA establishes a TWA exposure limit for benzene of 1 ppm for an 8-hour workday. According to NIOSH, the limit is 0.1 ppm for a 10-hour workday. ACGIH sets the limit at 0.1 ppm for an 8-hour day. These limits are established for workplace environments. There is no threshold limit set for continuous exposure such as would occur in residences. However, the Environmental Protection Agency (EPA) estimates that a lifetime exposure to 4 ppb (0.004 ppm) of benzene in air would result in one additional case of leukemia per 10,000 people exposed (Gordian and Guay, 1995).

Preliminary studies performed by the Alaska Department of Environmental Conservation (ADEC) during the winter of 1992-93 suggest that, in some locations in Fairbanks, concentrations of benzene in indoor air are high enough to pose a health risk. The ADEC measured benzene concentrations well above the 0.1 ppm limit in garages, with the concentration being as high as 0.35 ppm in some garages. In residences and public buildings, the ADEC found benzene concentrations from 1 to 51 ppb, with a mean of 6 ppb in December 1992 and 20 ppb in February 1993. The ADEC study showed a strong positive correlation between concentrations of benzene and methyl tertiary butyl ether (MTBE), an oxygenate added to gasoline during that winter. Since there is no large industrial source of benzene pollution in Fairbanks, the ADEC suggests that gasoline is the most likely source of benzene in the air in Fairbanks. Benzene can enter the air from

evaporation of gasoline as well from automobile exhaust. Cigarette smoke is also a significant source of individual benzene exposure (Gordian and Guay, 1995), but the effect of secondary smoke on indoor benzene levels has not been well established.

An extensive study of air pollutants including benzene was conducted in Valdez, in part to determine the effect of the oil pipeline terminal emissions on the exposure to residents of Valdez. Air was sampled simultaneously indoors and outdoors, and tracer gases were released from the terminal to determine the concentration of pollutants that were due to releases from the terminal. This study determined that personal exposure to pollutants such as benzene was dominated by indoor sources. Concentrations of benzene were significantly higher in homes than outdoors (an average of about 2.6 times higher), and most people spent more time indoors than outdoors. The authors of the Valdez Air Health Study report cited similar results from a large-scale EPA study conducted in 1987 in various locations in the lower 48 states. Although terminal emissions contributed 26% of the outdoor concentrations of pollutants in residential areas in Valdez, they only contributed 9% of indoor concentrations and about 11% of a person's total exposure to benzene. The contributions of terminal emissions were determined during 1990-91, before emission controls were installed at the terminal in 1994, so the contributions of terminal emissions to a person's exposure are probably even less now than they were at the time of the study. Mean indoor concentrations of benzene measured in Valdez in the summer were 2.5-6.3 ppbv, with a maximum of 66 ppbv. In the winter, indoor concentrations were higher, with means of 4.4-9.1 ppbv and a maximum of 72 ppbv. Differences between homes were observed for indoor concentrations, but not for outdoor

concentrations. These results suggest that sources of chemicals within the home are the major factor influencing personal exposure to benzene. The authors of the Valdez study conclude that the 70-year lifetime cancer risk from total benzene exposure is less than 180 chances in one million, which was not considered a significant health risk by the medical and toxicological experts who evaluated the exposure. This risk can be compared to a background cancer rate of 1 out of 4 from all causes including diet, smoking, and lifestyle (Goldstein et al, 1992).

The standard method for determining the concentration of benzene in air involves drawing a known volume of air through a charcoal adsorption tube (a small glass tube filled with charcoal) which traps the benzene vapors onto the charcoal. The benzene is then desorbed with carbon disulfide by transferring the charcoal to a small vial containing a known amount of carbon disulfide. The benzene partitions into the carbon disulfide and the resulting solution is then decanted. The concentration of benzene in the solution is determined with a gas chromatograph equipped with a flame ionization detector or mass spectrometer (Lodge, 1989). Because carbon disulfide is a very flammable substance to work with, it is desirable to develop a method that uses a different solvent. In undergraduate chemistry classes, students have used methylene chloride as an alternate solvent with moderate success (Jaffe, 1997).

This project has several objectives:

- to improve the charcoal tube method using methylene chloride as the solvent by better quantifying experimental factors such as flow rates and efficiencies, and by exploring the effects of several variables (the type of adsorbent used in the tube and the duration of the sonication period) on extraction efficiency.
- to sample air in homes in Fairbanks for benzene.
- to identify likely sources of benzene within the home.
- to compare three sampling methods (charcoal tubes, thermal desorption tubes, and badges) in an effort to determine which is most appropriate for use in future studies.

The charcoal tubes and thermal desorption tubes are both active sampling methods which involve pumping air through the tubes, with the method of analysis of the resulting sample being different. The badges are a passive sampling method during which benzene adsorbs onto charcoal pads via diffusion, with analysis of the charcoal pads being similar to that of the charcoal tubes. These three methods of sampling are described in detail in the *Materials and Methods* section.

Based upon the above objectives, I tested whether benzene would be detected in homes in Fairbanks, and what would be the highest concentrations found in homes in relation to the potential benzene sources located within the home (or the attached garage). I expected that homes which had the greatest number of vehicles stored in an attached garage would have the highest concentration of benzene. I also hypothesized that the extraction efficiency for the charcoal tubes could be maximized by adjusting variables

related to the extraction method, and that one of the three sampling techniques would be most appropriate for this type of study.

The null hypotheses include: (1) Benzene concentrations within homes in Fairbanks are below the detection limit for this method. (2) The concentration of benzene does not depend on the type or number of sources of benzene within the home or its attached garage. (3) The extraction efficiency for charcoal tubes does not depend on the type of adsorbent used in the tube or on the duration of the sonication period. (4) The three sampling techniques are equally effective.

Because other studies have shown that sources of benzene within the home are a major factor in determining a person's exposure, this study focussed on residential settings. Cigarette smoke as a potential source of benzene is not part of this study, so it was expected that most benzene found in the home would come from items typically stored in a garage, such as gasoline in vehicles and small engines, paints and stains, solvents, and glues. Sampling sites were therefore limited to homes with attached garages and with no smokers in the household.

Chapter 2

MATERIALS AND METHODS

At the outset, method development work focussed on a variation of the standard method using charcoal tubes, with methylene chloride as the solvent. Once the method development phase was complete, actual sampling began. At each site, three sampling techniques were used: charcoal tubes, thermal desorption tubes, and badges.

2.1 Sampling Apparatus

When sampling air with charcoal tubes, air is drawn through the tube with an electric pump, using the apparatus shown in Figure 1. As air is drawn through the tube, benzene in the air is adsorbed onto the solid in the tube. The adsorbent tube is held in a vertical position during sampling to prevent the solid within from shifting during sampling, possibly creating air channels through which air could flow more readily without benzene being adsorbed as effectively. In order to avoid possible adsorption of benzene or contamination of the air sampled by components of the sampling system, air being sampled flows through the tube first, before flowing through any other parts of the sampling system. This arrangement also ensures that the open end of the tube being used to sample air is at atmospheric pressure. A rotameter is used to measure the sampling flow rate (the rate, in L/min, at which air is drawn through the tube), and a vacuum gauge is used to measure the pressure drop across the tube. A needle valve is used to control the sampling flow rate. The pump then vents the air to the atmosphere. The sampling

Figure 1: Sampling Apparatus

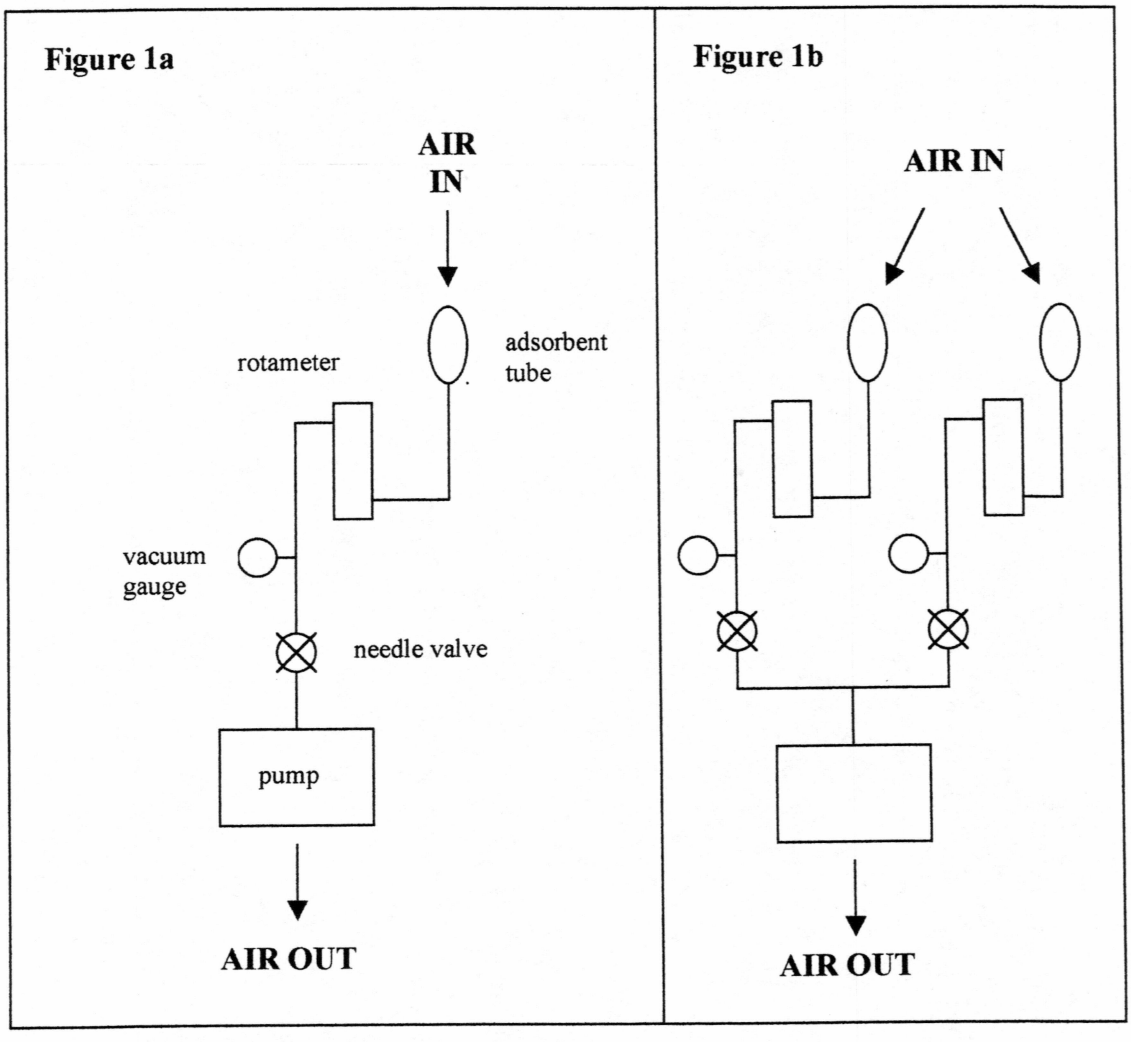

Figure 1: The apparatus used to sample air with one tube (1a) or with two tubes simultaneously at different flow rates (1b).

duration is recorded, as are the atmospheric pressure and temperature. The components of the system are connected by Teflon or thick-walled Tygon tubing in the order described above. During the method development phase of the project, only one sample tube was connected to the pump at a time. During actual sampling, two tubes were

connected to the pump at the same time, with the two tubes at different flow rates (1.0 and 0.1 standard liters per minute, SLPM). At the end of the sampling period, tubes are sealed with plastic caps and stored at room temperature (20-25 °C) until they can be processed, usually within 1-2 weeks.

Sampling duration and rotameter flow rate are used to calculate the volume of air sampled. Each rotameter was calibrated using a bubble flow meter to determine standard flow rates. The calibration curve was used to determine the standard rotameter reading, which was then corrected for the pressure drop across the tube and the slight differences between the conditions during calibration and the conditions during sampling, using the following equation suggested by Omega (Omega, 1992):

$$\text{standard flow rate} = (\text{standard rotameter reading})\sqrt{\left(\frac{P_{atm} - P_{vac}}{P_{cal}}\right)\left(\frac{T_{cal}}{T_{actual}}\right)}$$

Where P_{atm} = the average absolute atmospheric pressure during sampling

P_{vac} = the pressure drop (differential) across the tube (the vacuum gauge reading)

P_{cal} = the absolute pressure at which the rotameter was calibrated

T_{cal} = the temperature (K) at which the rotameter was calibrated

T_{actual} = the average temperature (K) during sampling

Extraction efficiencies were compared for two types of adsorbent tubes manufactured by ORBO: the standard charcoal tubes, filled with activated coconut charcoal (ORBO model # 32 small) and Carbotrap tubes (ORBO model # 101). Both types of tubes have a bed weight of 100 mg in the main portion of the bed and 50 mg in

the breakthrough portion, and are of a 20/40 mesh particle size. Lodge (1989) states that the capacity of the main bed for benzene is 6 mg, although this could decrease with the presence of other organic compounds in the air being sampled. The breakthrough bed can be analyzed to determine whether or not the capacity of the main bed was exceeded. According to Lodge (1989), the sample is still valid (no significant sample loss occurs) as long as the amount of benzene in the breakthrough bed is less than 25% of that found in the main bed. If this condition is met, the total benzene in the two beds (the main bed and the breakthrough bed) is used as the amount of benzene present in that sample. The charcoal tubes were found to have a much higher extraction efficiency with methylene chloride than the Carbotrap tubes, and were therefore used for all subsequent samples. (See Table 1, section 3.1.)

The thermal desorption tubes, produced by SUPELCO, were glass tubes (4 mm i.d. x 6 mm o.d. x 11.5 cm long) filled with Carbotrap 300 adsorbent. The thermal desorption tubes had air pumped through them in a manner similar to that described for the charcoal tubes, with a few differences. Much slower flow rates were used (4 and 16 mL/min), so the pressure drop across the tube was not measured during sampling (since it is not significant at such low flow rates). The flow rate was set and maintained by the pump itself instead of using a needle valve and rotameter. All sampling with the thermal desorption tubes was conducted in collaboration with Maggie Isbell.

The passive-sampling badges used were 3M's model 3520 organic vapor diffusion monitor, which contains a charcoal adsorbent pad in both a primary and a secondary section, the secondary section functioning like the breakthrough bed in the

charcoal tubes. Each charcoal pad has about 160 mg of activated carbon in a Teflon matrix (3M Company, 1997). The capacity of each section for benzene is 22 mg, and the sample is considered valid as long as the amount of benzene collected by the secondary section is less than or equal to 50% of the amount collected by the primary section (3M Company, 1996). The badges were simply clipped to a location near the other sampling devices, one attached to the charcoal tube sampler and the other attached to the thermal desorption tube sampler. Once sampling with the badges was complete, the primary and secondary sections were separated and sealed with plastic caps, then stored in a sealed can at room temperature until analysis (usually within two weeks).

The sampling rate for the badges is controlled by molecular diffusion (3M Company, 1997), and has been determined by scientists at 3M to be 35.5 mL/min for benzene, standardized to 25 °C and 1 atm pressure (3M Company, 1996). This sampling rate, along with the amount of time the air was sampled, is used to calculate the volume of air sampled. For samples collected at temperatures other than 25 °C, the volume of air sampled can be corrected for temperature differences using correction factors published by 3M. The correction factors amount to a 1% correction for every 6 °C above or below 25 °C, with correction factors being less than 1 for temperatures above 25 °C and greater than 1 for temperatures below 25 °C. No correction is needed for differences in pressure (3M Company, 1996). Since all samples collected for this study were taken at average room temperatures within three degrees of 25 °C, no temperature corrections were applied.

2.2 Sample Analysis

Once the charcoal tube sample has been collected, the adsorbent is removed, with the main bed and breakthrough portion processed separately. Analysis of the breakthrough portion allows one to determine whether or not the capacity of the main bed was exceeded.

During the method development phase of the project, samples were analyzed as follows. The adsorbent is placed in a small (2 mL) glass vial. One mL of methylene chloride is added to the vial, and the vial (sealed with a Teflon-coated cap and wrapped with Parafilm) is sonicated for a period of time. Sonication times of 30 minutes and 4 hours were compared. For reasons that will be discussed in the *Results* section, a sonication time of 30 minutes was determined to be preferable, and was used for all subsequent samples.

After sonication, the vials are allowed to cool to room temperature. Using a Pasteur pipette, the liquid is then transferred from the sonication vial to an autosampler vial. A small piece of glass wool is inserted into the sonication vial to prevent any solid from entering the pipette. Samples are then analyzed using a gas chromatograph equipped with a mass spectrometer (GC-MS). Five standard solutions with concentrations in the range of 0-35 mg/L are prepared and analyzed along with the samples.

The GC-MS used is a Hewlett Packard HP5890 series II-plus interfaced to a HP 5972 mass selective detector which is a quadrupole mass spectrometer. The instrument is controlled by a personal computer (PC).

The analysis method uses the following GC conditions. The column is a 30 m x 0.25 mm i.d. capillary column with a stationary phase of 5% phenyl dimethylsiloxane. This is a weakly polar column which separates species primarily by their boiling points. The injection volume is 1 μL using a robotic autosampler. A split injection is used, with a split ratio of 60:1. The injection temperature is 275 °C. The oven program consists of 4 minutes at 32 °C, a ramp to 80 °C at 10 °C/minute, a ramp to 100 °C at 20 °C/minute, and a ramp to 150 °C at 30 °C/min, then 1 minute at 150 °C. The solvent delay time is 2.80 minutes (for methylene chloride). The detector temperature is 300 °C. For most analyses, the autosampler tray was cooled to 5-10 °C to minimize evaporation, in case samples needed to be analyzed again later.

When actual sampling took place, the method was modified slightly in an effort to further improve extraction efficiency. A series of three extractions was carried out on each sample, using 0.75 mL of solvent each time. The extraction itself was carried out in 2 mL micro-reaction vessels with a conical base, instead of the flat-bottomed vials that were used previously, to minimize the amount of liquid remaining in the vial after each extraction. The extraction vials had caps with Teflon-faced neoprene septa. Vials were not wrapped with Parafilm during sonication. Glass wool was no longer used during the pipetting of liquid from the extraction vial, but care was taken to avoid getting any solid in the pipet. The liquid removed after each extraction was added to a previously labeled and massed autosampler vial, with the liquid from all three extractions added to the same vial. The vial was again massed after the three extractions were complete in order to determine the total mass (and thus volume) of liquid extracted. It is assumed that the

amount of benzene remaining in the extraction vial after the third extraction is negligible, or at least that the relative amount remaining is consistent and can be accounted for with the overall extraction efficiency. A permeation oven was not available during this latter part of the project, so actual extraction efficiency of this method was not determined.

Analysis of the badges was similar to the method described for charcoal tubes, with slight modifications. To prepare the sample for analysis, the charcoal pad was removed from the badge with clean tweezers, cut into four pieces with clean scissors, and placed in an extraction vial. The sample was then processed using the method previously described for the charcoal tubes.

When sampling took place, extracted solutions were analyzed using a gas chromatograph equipped with a flame ionization detector (GC-FID). The GC-FID used is a Hewlett Packard HP6890 Series GC System. The instrument is controlled by a PC. The column is a 30 m x 0.45 mm i.d. capillary column with an EC-WAX carbowax coating and a film thickness of 1.0 μm. This is a very polar column. The injection volume is 1 μL using a robotic autosampler. A splitless injection is used, and the injection temperature is 275 °C. The oven program consists of 3 minutes at 37 °C, a ramp to 200 °C at 20 °C/minute, then 1 minute at 200 °C. The detector temperature is 250 °C. The autosampler tray was cooled to 5-10 °C.

Analysis of a set of ten standard solutions of benzene in methylene chloride over a range of 0-200 mg/L showed that the GC-FID response was linear over that range. During analysis of samples, an 80 mg/L standard solution was run at the beginning and

end of each set of samples, and was repeated after every five samples. A blank (pure solvent) was also analyzed with each set of samples.

The standard solutions were used to produce a calibration curve, which was then used to determine the concentration of benzene in the solution produced from each sample. Early in the project, when only one extraction was carried out on each sample, the volume of methylene chloride added to the charcoal (1 mL) and the concentration of benzene in the solution were used to determine the amount of benzene (in μg) present in the total amount of solution, and thus the amount of benzene recovered from the charcoal. Later, when three extractions were carried out for each sample, the mass of solution delivered to the autosampler vial (after all three extractions were complete) and the density of methylene chloride were used to determine the volume of solution in the vial. The volume of solution and the concentration of benzene in the solution were then used to calculate the amount of benzene (in μg) present in the vial, and thus the amount of benzene recovered from the charcoal.

Once the amount of benzene recovered has been determined, the efficiency of the method can be used to calculate how much benzene was actually collected during sampling. An efficiency of 100% was assumed during all calculations for charcoal tube samples collected during the sampling of homes. Since the actual efficiency is most likely less than 100% (for reasons to be discussed in the *Results* section), actual benzene concentrations in the air sampled are probably higher than those reported. A permeation oven can be used to generate data which will allow one to determine the actual efficiency of the method, and thus to re-calculate a more accurate benzene concentration for each air

sample. For badge samples, an efficiency of 32% was used to calculate the amount of benzene present in the air sampled. This efficiency was determined by loading a solution of benzene in hexane directly onto badges, as will be explained later.

The mixing ratio (concentration) of benzene in the air sampled was determined by converting the mass of benzene to moles (using the molar mass of benzene), and the volume of air to moles (using the ideal gas law), then determining the ratio of moles of benzene to moles of air. The mixing ratio of benzene is reported as parts per billion by volume (ppbv), since the ratio in terms of moles is effectively the same as the ratio in terms of volume for gases.

A thermal desorption tube is analyzed by connecting it directly to the GC-FID and heating it to volatilize the substances that had been adsorbed. The vapors then pass into the GC-FID for analysis.

2.3 Determination of Extraction Efficiency for Charcoal and Carbotrap Tubes

To determine the extraction efficiencies of charcoal and Carbotrap tubes, tubes are loaded with a known amount of benzene. To accomplish this, a permeation tube containing benzene is placed in a permeation oven, which is maintained at a constant temperature (50 °C). Breathing quality air (which has first been passed through a charcoal scrubber to remove benzene and other organic vapors) is passed through the oven at a fixed rate (0.33 SLPM). The permeation rate is then determined by measuring the rate of change of mass of the tube over a period of at least one week. Additional breathing air (also scrubbed) is mixed with the air from the oven. The rate of flow of

dilution air is measured and can be adjusted to produce different concentrations of benzene. This air is then sampled as described previously, with the sampling flow rate being less than the total flow coming from the oven (see Figure 2). Excess air from the oven is vented to a fume hood. This way, the sampling is done at atmospheric pressure. The amount of benzene loaded onto the tube can then be calculated using the following equation:

$$\text{mass of benzene loaded} = (\text{permeation rate})\left(\frac{\text{sampling flow rate}}{\text{total flow rate}}\right)(\text{sampling duration})$$

The efficiency of the extraction method can then be determined by comparing the amount of benzene recovered to the amount loaded, using the equation:

$$\text{efficiency} = \frac{\text{mass benzene recovered}}{\text{mass benzene loaded}} \times 100\ \%$$

Once the charcoal tubes and a 30-minute sonication time were selected, additional tubes were loaded with different amounts of benzene by sampling air from the permeation oven with various concentrations of benzene (5-23 ppbv) for different amounts of time (1.5-15 hours). This was done to determine whether sampling time or concentration of benzene affect extraction efficiency. Several of these samples were extracted a second time by adding another 1 mL of solvent to the charcoal after the first extraction was complete, then processing the charcoal as for the first extraction. The solution from the second extraction was analyzed separately from that obtained from the first extraction.

Figure 2: Permeation Oven Set-up

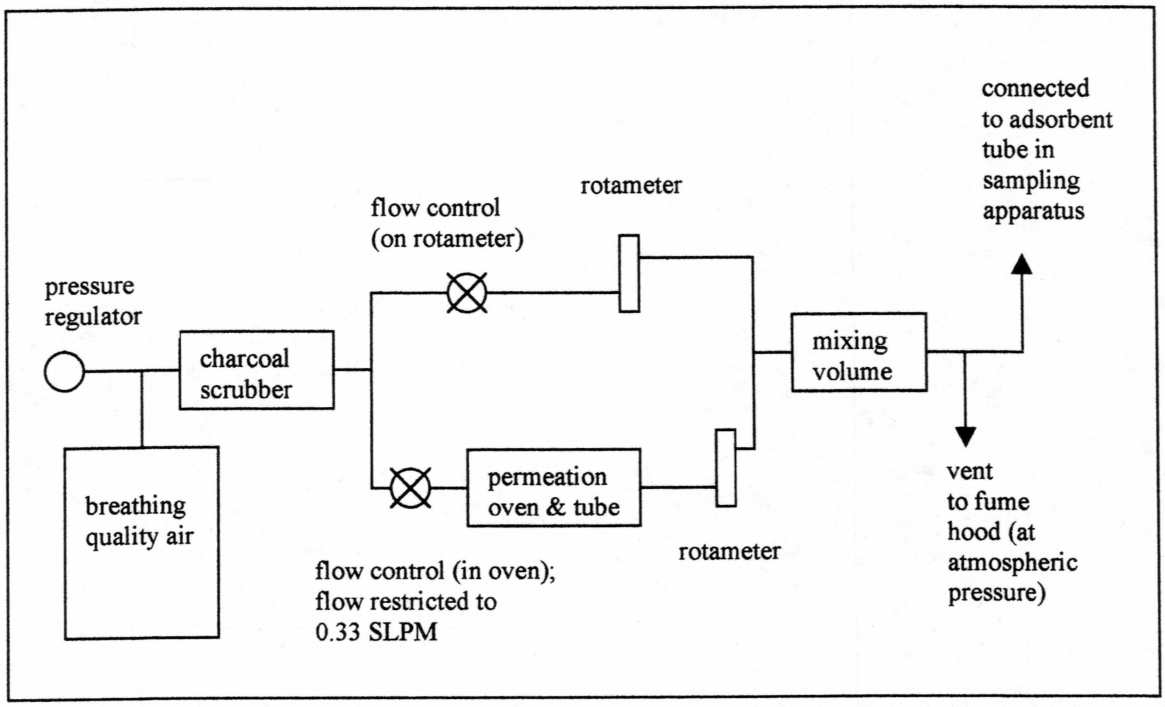

Figure 2: The diagram above shows the permeation oven set-up used to load tubes with benzene in order to determine efficiency.

2.4 Determination of Extraction Efficiency for Badges

To determine the extraction efficiency for the badges, four badges were loaded with a known amount of benzene using a procedure similar to that described by 3M scientists (3M Company, 1996). To load a badge with benzene, the plastic ring and white film were removed from the front of the monitor and a 2.5 cm diameter piece of filter paper was placed on top of the spacer plate above the charcoal pad inside the primary section of the badge. The elution cap was immediately snapped to the top of the monitor to seal the badge. The badge assembly was then massed. A 10.0 mL solution of

202 μL benzene in hexane was prepared, and a 5 μL portion of this solution was added to each badge assembly through the center port of the elution cap using a pipet. The port was immediately sealed, and the badge assembly was again massed to determine how much solution was actually delivered to the badge. The badge was then allowed to sit for 21 hours, to allow the benzene to diffuse from the filter paper onto the charcoal pad. Next, both sections of the badge were processed and analyzed as usual.

The mass of benzene loaded onto the badge can be calculated as follows. First, the density of the solution is calculated as shown below. This calculation assumes that the volume of the solution is equal to the sum of the volumes of the two liquids, which is a reasonable assumption since the volume of benzene is so small relative to the volume of the solution.

$$\text{density of solution} = \frac{(\text{volume benzene})(\text{density of benzene}) + (\text{volume hexane})(\text{density of hexane})}{(\text{volume of solution})}$$

$$\text{density of solution} = \frac{(0.202\ \text{mL})(0.87865\ \text{g/mL}) + (9.8\ \text{mL})(0.6603\ \text{g/mL})}{(10.0\ \text{mL})} = 0.6648\ \text{g/mL}$$

The mass of solution added to a badge is determined by finding the difference in mass of the badge before and after the solution is added to the badge, and was approximately 0.0030 g each time. Next, the volume of solution added is calculated using the mass and density of the solution. The volume of benzene added to the badge can then be calculated using a simple ratio:

$$\frac{0.202\ \text{mL benzene}}{10.0\ \text{mL solution}} = \frac{\text{volume of benzene added}}{\text{volume of solution added}}$$

The mass (in μg) of benzene added to the badge is then calculated using the density of benzene (0.87865 g/mL):

$$\mu g \text{ benzene loaded} = (\text{mL benzene added})(0.87865 \text{ g/mL})(10^6 \mu g/g)$$

To determine the efficiency, the mass of benzene recovered (as determined by GC-FID analysis) is compared to the mass of benzene loaded:

$$\text{efficiency} = \frac{\text{mass of benzene recovered}}{\text{mass of benzene loaded}} \times 100\%$$

2.5 Sampling of Homes

During the summer of 1998, eight homes with attached garages were sampled for benzene. The purpose of the sampling was twofold. First, we wanted to sample actual sites to compare the three methods of sampling. In addition, the sampling would serve as a baseline measurement for benzene levels in the summer. Houses with attached garages were selected because it was expected that benzene levels would be relatively low in the summer, when people typically have windows open much of the time, and we expected that homes with attached garages would generally have higher concentrations of benzene than would homes without attached garages.

At each site, we inspected the garage for items stored there, looking particularly for possible sources of benzene such as vehicles, small engines (lawnmowers, chain saws, etc.), furnaces, paints, glues, and solvents. We also interviewed the homeowner about other relevant information, such as possible sources of benzene not readily visible in the garage, items stored in other locations in the home, the presence of smokers in the

home, whether the home had a ventilation system, and whether windows were open or closed during sampling. There were no smokers in any of the homes sampled. None of the homes sampled had ventilation systems. At each site, two charcoal tubes were set up with flow rates of 1.0 and 0.1 SLPM, two thermal desorption tubes were set up with flow rates of 4 and 16 mL/min, and two badges were set up. One charcoal tube and one badge were opened at each site and immediately sealed, to serve as blanks for that site. Sampling times were measured to the nearest minute and varied from 11 to 12 hours.

The main beds from all charcoal tubes and the primary sections from all badges were analyzed. In addition, two breakthrough beds from charcoal tubes were analyzed—one was randomly selected from each week's samples collected at the higher flow rate. The secondary sections from two badges were also analyzed—from each week's samples, one (of the two from that site) was randomly selected from the site shown to have the highest benzene concentration based on analysis of the charcoal tubes. For comparison, solutions (in methylene chloride) of gasoline and of a gasoline-oil mixture (taken from a chainsaw) were analyzed on the GC-FID. In addition, samples from the main beds of the high-flow charcoal tubes, as well as the gasoline and gasoline-oil solutions, were analyzed qualitatively on the GC-MS to identify the substances present. Between GC-FID and GC-MS analysis, solutions were left in the autosampler vial with a new septum in the cap and stored in a freezer (-20 °C). Solutions were warmed to room temperature and mixed before GC-MS analysis. Solutions were diluted as necessary to prevent overloading the GC-MS detector.

Chapter 3

RESULTS

3.1 Comparison of Charcoal and Carbotrap Tubes

An initial comparison of the two types of adsorbent tubes was carried out using a sampling flow rate of about 1.6 SLPM and a sampling time of 3-4 hours. Air sampled contained approximately 18 ppbv benzene. Extraction efficiencies for these conditions are summarized in Table 1.

Table 1: A Comparison of Charcoal and Carbotrap Tubes

	Adsorbent Type	
	Charcoal	Carbotrap
Trial 1	63.5 %	9.7 %
Trial 2	62.3	14.2
Trial 3	55.0	13.1
Trial 4	57.9	10.1
Mean	59.7	11.8
Standard Deviation	3.9	2.2

Table 1: Extraction efficiencies for two types of adsorbent tubes.

Extraction efficiencies are much greater for the charcoal tubes. A relatively large amount of benzene was found in the breakthrough portion of each of the Carbotrap tubes (31-57% of the amount found in the breakthrough bed), while no benzene was found in

the breakthrough portions of the charcoal tubes. No benzene was found in any of the blanks that were processed.

3.2 Comparison of Sonication Times

A comparison of 30-minute and 4-hour sonication times was carried out using a sampling flow rate of about 1.7 SLPM and a sampling time of 2.5 hours. Air sampled contained approximately 23 ppbv benzene. Extraction efficiencies for these conditions are summarized in Table 2.

Table 2: A Comparison of Sonication Times

	Sonication Time	
	4 hours	30 minutes
Trial 1	56.6 %	57.0 %
Trial 2	58.8	52.1
Trial 3	62.8	53.2
Trial 4	59.6	54.7
Mean	59.5	54.3
Standard Deviation	2.6	2.1

Table 2: Extraction efficiencies for two different sonication times: four hours compared with thirty minutes.

The efficiency appears to be a bit higher for the 4-hour sonication time. However, there was also a noticeable loss of liquid after the 4-hour sonication time. The small difference in efficiency could be due to the evaporation of solvent from the vials. One

breakthrough bed and one blank were also analyzed, and no benzene was found in either the breakthrough bed or the blank.

3.3 Effect of Sampling Time and Concentration of Benzene on Efficiency

To determine whether sampling time or concentration of benzene affect extraction efficiency, tubes were loaded with air of different concentrations of benzene (5-23 ppbv) and for different amounts of time (1.5-15 hours). A sampling flow rate of about 1.7 SLPM was used. Several samples were extracted a second time to determine if multiple extractions would increase efficiency. Extraction efficiencies for these conditions are summarized in Table 3. Efficiencies for single extractions are illustrated in Figure 3.

Efficiencies for single extractions are similar for all sampling times and benzene concentrations. Several samples were extracted a second time, as indicated in Table 3. In all three cases, the second extraction recovered additional benzene-- about 30-40% of the amount recovered in the first extraction. These calculations assume that all of the benzene recovered in the second extraction is additional benzene desorbed from the charcoal. It is likely that some of the benzene recovered in the second extraction was present in the small amount of liquid that remained in the charcoal after the first extraction. If this is the case, the total efficiencies that include the benzene recovered in the second extraction are higher than they should be. This could explain why these total efficiencies are greater than 100%.

Table 3: A Comparison of Sampling Times and Concentrations

Group Number	Sampling Time (hours)	Conc. of Benzene in Air (ppbv)	Single Extraction Efficiency (%)	Total Efficiency (%)
1	1.5	23.4	86.5	
1	1.5	22.9	84.4	
1	1.5	23.3	90.5	124
2	4.0	23.1	80.2	110
2	4.0	23.4	93.2	
2	4.0	22.9	86.1	
3	15.0	21.2	97.7	
3	15.0	21.6	74.8	
3	15.0	22.4	88.1	115
4	4.0	11.4	86.6	
4	4.0	11.5	87.5	
4	4.0	11.4	81.3	
5	4.0	5.7	86.0	
5	4.0	5.5	84.5	
5	4.0	5.6	81.5	

Table 3: Extraction efficiencies for a variety of sampling times and concentrations of benzene in the air sampled. Empty cells in the table indicate analyses that were not completed for those samples. Total efficiency is the sum of the efficiencies of the first and second extractions.

Two blanks were analyzed, one which sampled air flowing through the permeation oven (with no permeation tube in it) as well as the dilution air channels, and one which sampled air flowing only through the dilution air channels. No benzene was found in either blank.

The breakthrough beds for the three tubes loaded with the greatest amount of benzene were analyzed; one contained a small amount of benzene (less than 1% of the amount found in the main bed), while the other two contained no benzene.

Figure 3: Single Extraction Efficiencies

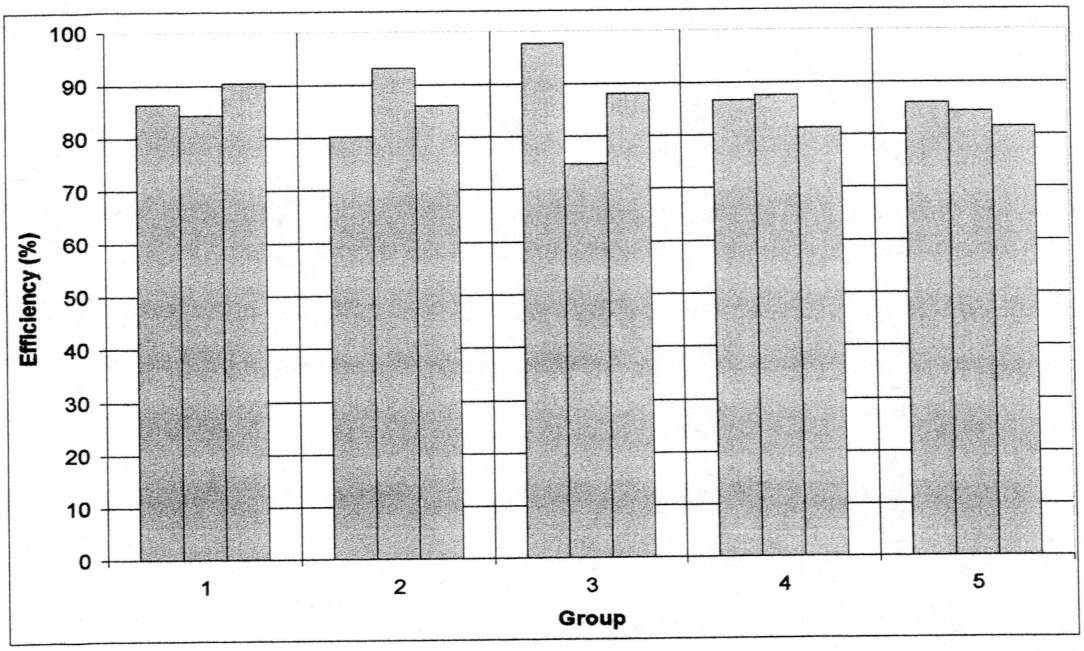

Figure 3: Extraction efficiencies for a variety of sampling times and concentrations of benzene in the air sampled. See Table 3 for the sampling time and benzene concentration used for each group. Efficiencies are for single extractions.

3.4 Permeation Rate

Figure 4 shows a graph of the mass of the permeation tube with respect to time. The slope of the graph represents the permeation rate. Each series (each set of points connected by a line) represents a period of time during which there was uninterrupted flow of gas through the permeation oven. On several occasions, the tank of air supplying the permeation oven ran out. These times are shown as breaks between series. The permeation rate for each series varies significantly, from 167 ng/min to 264 ng/min. There is more scatter between data points in series 3 and 4 than there is in series 2 and 5.

Figure 4: Determination of Permeation Rate

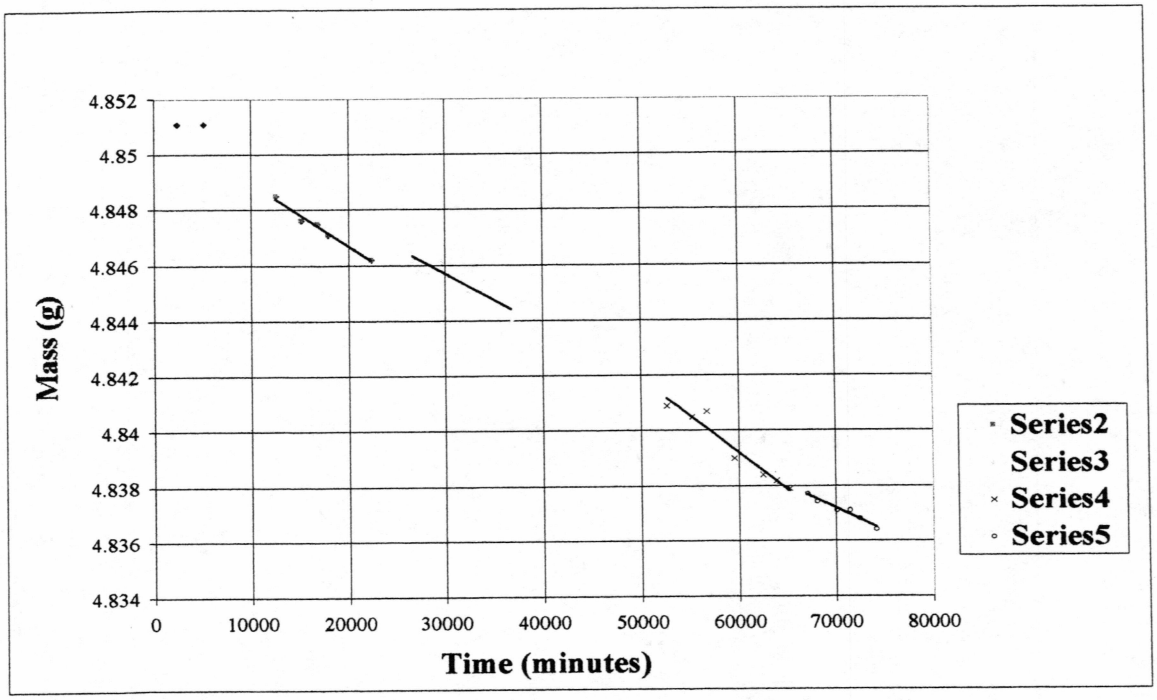

Figure 4: The slope of the graph of the mass of the permeation tube versus time is used to determine the permeation rate. Each series represents a period of time during which there was uninterrupted flow of gas through the permeation oven. Breaks between series represent periods of time during which there was an interruption in gas flow through the oven.

Series 2:	6/30-7/7/97	slope = 227 ng/min	$R^2 = 0.9768$
Series 3:	7/10-17/97	slope = 191 ng/min	$R^2 = 0.7984$
Series 4:	7/28-8/6/97	slope = 264 ng/min	$R^2 = 0.9434$
Series 5:	8/7-12/97	slope = 167 ng/min	$R^2 = 0.9512$

The variation in permeation rate creates a problem when determining extraction efficiency, because the permeation rate is used in calculating the amount of benzene loaded on each tube, which in turn is used in calculating the extraction efficiency. Using a larger permeation rate would result in a larger amount of benzene loaded and thus a smaller efficiency, while using a smaller permeation rate would result in a larger

efficiency. In determining the efficiencies for results reported previously in this thesis, the permeation rate used was generally that determined for the period of time during which those tubes were loaded. The results for the comparison of sampling times and concentrations (Table 3) used the permeation rate for the last series (series 5) when analyzing the results for all of these tubes, even though some of these tubes were loaded during the last two days of series 4 (8/5-6/97). This seemed like a reasonable choice for two reasons. First, the slope for series 4 was different from that of series 5 and appeared to be determined largely by the earlier points in the series. Using such different permeation rates for tubes being compared to each other did not seem reasonable. Second, the data points for days 8/5-6/97, when the tubes in question were loaded, seemed to fall on the line for series 5, so it seemed reasonable to use the slope of that line for those tubes.

3.5 Summary of Extraction Efficiencies for Charcoal Tubes

Table 4 summarizes the extraction efficiencies for all of the trials that used the method involving charcoal tubes and a 30-minute sonication period. Because of the issues related to the determination of the permeation rate, the extraction efficiencies have been calculated two ways. The first set of efficiencies in Table 4 uses the permeation rate determined for the period of time during which the tubes were loaded, with the rate used being shown in the table. Since it is expected that the permeation rate is actually constant, the efficiencies were re-calculated using the same permeation rate (167 ng/min) for all tubes. Although this value may not necessarily represent the actual permeation

Table 4: Summary of Extraction Efficiencies for Charcoal Tubes

Sampling Time (hours)	Using Conc. of Benzene in Air Sampled (ppbv)	Permeation Rate (ng/min)	Rate Shown: Single Extraction Efficiency (%)	Rate Shown: Total Efficiency (%)	Using Rate of 167 ng/min: Single Extraction Efficiency (%)	Using Rate of 167 ng/min: Total Efficiency (%)
3.9	18	191	63.5		72.6	
3.3	18	191	62.3		71.3	
2.8	18	191	55.0		62.9	
3.2	18	191	57.9		66.2	
2.5	23	264	57.0		90.1	
2.5	23	264	52.1		82.4	
2.8	23	264	53.2		84.0	
2.5	23	264	54.7		86.5	
1.5	37	264	54.7		86.5	
1.5	36	264	53.4		84.4	
1.5	23	167	90.5	124.3	90.5	124.3
4.0	23	167	80.2	109.6	80.2	109.6
4.0	37	264	59.0		93.2	
4.0	36	264	54.5		86.1	
15.0	34	264	61.8		97.7	
15.0	22	167	74.8		74.8	
15.0	22	167	88.1	114.9	88.1	114.9
4.0	11	167	86.6		86.6	
4.0	12	167	87.5		87.5	
4.0	11	167	81.3		81.3	
4.0	6	167	86.0		86.0	
4.0	6	167	84.5		84.5	
4.0	6	167	81.5		81.5	
Mean			68.7		82.8	
Std. Dev.			14.4		8.4	
Range			52.1-90.5		62.9-97.7	

Table 4: Extraction efficiencies are shown for both variable and fixed permeation rates. All tubes were loaded and analyzed using the same method (charcoal tubes processed with a 30-minute sonication period). Empty cells in the table indicate analyses that were not completed for that sample.

rate, using the same value for all calculations allows one to compare the results without the effect of different permeation rates. The rate chosen is that determined for the final series of measurements with the permeation oven and is the smallest of the rates determined, which would result in the highest efficiencies. If the actual rate is greater than 167 ng/min, efficiencies would be less than those shown in Table 4. When a fixed permeation rate is used to calculate efficiencies, the relative standard deviation of the resulting efficiencies is less than when a variable permeation rate is used.

A wide range of extraction efficiencies, about 50-100%, was determined for the method used during the early part of this study. The actual efficiency depends a great deal on the choice of permeation rate. Because a permeation oven was not available during the latter part of this study, a better determination of permeation rate (and thus efficiency) was not undertaken. Also, in the latter part of this study, the method was modified to include three extractions, so the efficiency for the final method is assumed to be higher than that determined for the single-extraction method discussed earlier.

3.6 Determination of Extraction Efficiency for Badges

The efficiency of the badges, as determined by loading a solution of benzene in hexane directly onto several badges, is given in Table 5. Efficiencies for the four badges loaded ranged from 26% to 36%, with an average of 32%.

Table 5: Extraction Efficiency for Badges

Badge	Efficiency (%)
1	36
2	35
3	30
4	26
Mean	32
Std. Dev.	5

Table 5: Extraction efficiency for passive-sampling badges as determined by loading a solution of benzene in hexane directly onto the badge.

3.7 Sampling of Homes

The results of sampling homes during the summer of 1998 are summarized in Table 6 and illustrated in Figure 5. The concentration of benzene in air inside each home is given for each of the three sampling methods, with two measurements for each method, giving a total of six measurements of the concentration of benzene for each site. At each site, a blank badge and a blank charcoal tube were processed; none of these blanks were found to contain any measurable benzene. Two breakthrough beds of charcoal tubes and two secondary sections of badges were also analyzed and were found to contain no measurable amounts of benzene. Thermal desorption tube results are a summary of analyses performed by Maggie Isbell.

The most reliable results are probably those from the thermal desorption tube samples, because of problems associated with the determination of efficiencies for the charcoal tubes and badges.

Table 6: Residential Benzene Concentrations

	Concentration of Benzene in Air (ppbv)							
	Site #							
Sampling Method	1	2	3	4	5	6	7	8
Charcoal Tube #1 (low flow)	0.0	31.3	0.0	22.4	3.9	5.3	4.0	3.3
Charcoal Tube #2 (high flow)	0.4	46.9	0.5	31.0	9.1	8.3	3.9	5.8
Badge #1	0.0	61.7	0.0	25.4	0.0	0.0	0.0	0.0
Badge #2	0.0	66.7	0.0	29.6	0.0	0.0	0.0	0.0
T. D. Tube #1 (low flow)	0.9	76.5	0.1	38.3	3.0	3.7	11.5	7.9
T. D. Tube #2 (high flow)	1.4	67.6	0.8	30.2	7.2	7.3	10.9	9.6
Mean Benzene Concentration (average of all 6 samples)	0.5	58.5	0.2	29.5	3.9	4.1	5.1	4.4
Mean Benzene Concentration for Thermal Desorption Tubes	1.2	72.1	0.5	34.3	5.1	5.5	11.2	8.8
Relative Benzene Conc.	low	high	low	high	med	med	med	med

Table 6: Benzene concentrations in indoor air at eight homes in Fairbanks, sampled during the summer of 1998. (High $\geq$ 20 ppbv; medium $\geq$ 4 ppbv; low $\geq$ 0 ppbv.) Thermal desorption tube results are probably the most reliable.

The benzene concentrations in Table 6 and Figure 5 that are based on the charcoal tube samples were calculated assuming an efficiency of 100%. If the efficiency is less than 100%, the benzene concentrations for the charcoal tube samples would be higher than those indicated. Based on the early efficiency studies, the efficiency is certainly not less than 50%, which means that the benzene concentrations would at most be double those shown.

The benzene concentrations in Table 6 and Figure 5 that are based on the badge samples were calculated using an efficiency of 32%, which was determined by loading a solution of benzene in hexane directly onto the badges. If the actual efficiency is different from this estimate, the benzene concentrations for the badge samples would be

Figure 5: Residential Benzene Concentrations

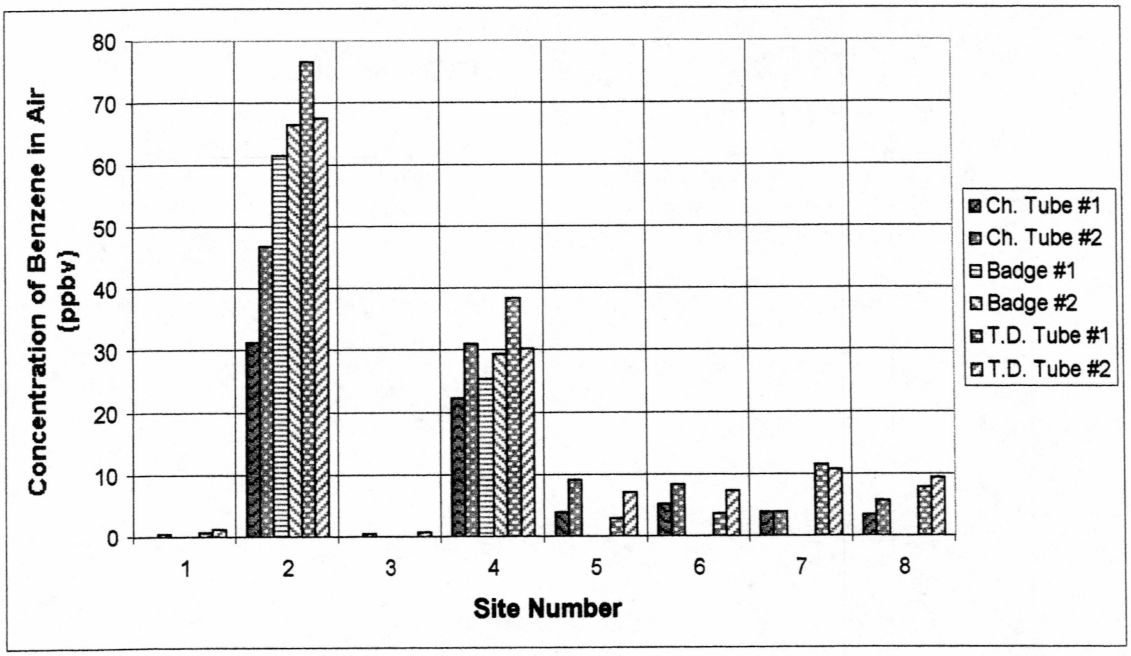

Figure 5: Benzene concentrations in indoor air at eight homes in Fairbanks, sampled during the summer of 1998. Badge samples that appear to be missing are zeroes (no benzene was found, or GC-FID peaks were too small to integrate). Thermal desorption tube results are probably the most reliable.

different than those indicated— higher concentrations if the efficiency is less than 32%, lower if efficiency is greater than 32%.

The benzene concentrations determined from analysis of the low-flow charcoal tubes and the badges have a high degree of uncertainty, because the peaks observed in the GC-FID chromatograms were very small and therefore difficult to integrate accurately.

Benzene concentrations at all sites were less than 100 ppbv. The highest concentration is about 70 ppbv, and most sites have concentrations at or above 4 ppbv. Although there is some variation between the benzene concentrations determined using

different methods at the same site, there is agreement between the charcoal tube and thermal desorption methods in terms of the relative benzene concentration at each site. For high concentrations of benzene, the badge method agrees with the other two methods.

Figure 6 shows chromatograms from the GC-FID analysis of an air sample taken with the high-flow charcoal tube at site 2, the site with the highest concentration of benzene, and of a gasoline-oil mixture taken from a chainsaw. The chromatograms of air samples from all eight sites showed many similarities in the locations and relative heights of peaks. The chromatograms for gasoline and for the gasoline-oil mixture were not noticeably different. Note that the chromatogram for site 2 has peaks with retention times and relative heights that match many of the peaks present in the gasoline-oil chromatogram. The large peak at 7.4 minutes and the triplet of peaks at 8.3 minutes are especially noticeable as present in both chromatograms. However, there are also peaks in the sample chromatogram that are not found in the gasoline-oil chromatogram, such as the small peak at 8.1 minutes (just before the triplet). For comparison, chromatograms for blanks and standard solutions can be found in Figure 7. The large peak at 6 minutes represents the solvent. The benzene peak is located at 6.4 minutes, on the shoulder of the solvent peak. The gasoline-oil mixture was analyzed at a different time (7/27/98), when there was a peak at 7 minutes in the solvent chromatogram that had not been observed previously, and the benzene peak had moved more onto the shoulder of the solvent peak.

GC-MS analysis of the samples and of the gasoline solutions also showed that the majority of substances present in the samples were also present in the gasoline solutions.

Figure 6: Chromatograms of a Site 2 Sample and of a Gasoline-oil Mixture

Figure 6a: Site 2 sample; charcoal tube with high flow rate; analyzed 7/7/98

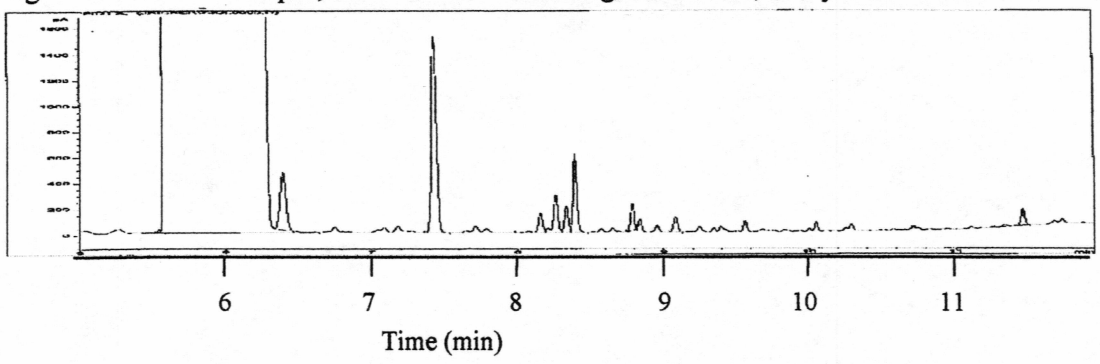

Figure 6b: gasoline and oil mixture taken from chainsaw; analyzed 7/27/98

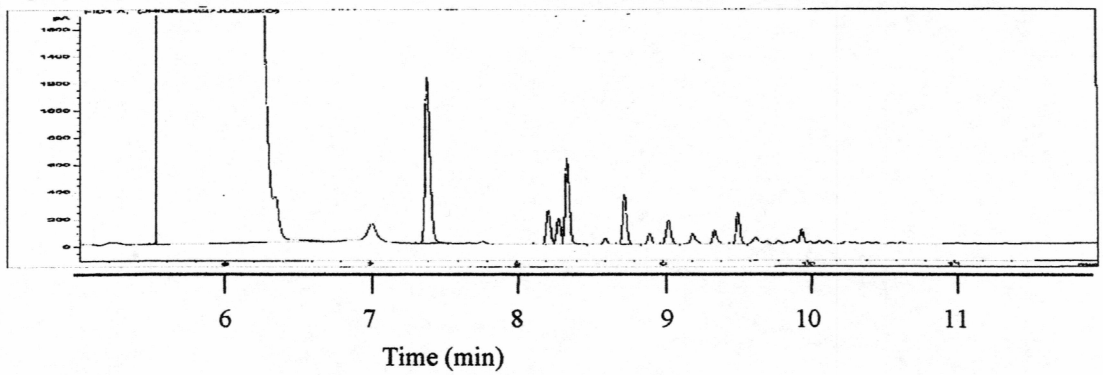

Figure 6: GC-FID chromatograms of an air sample taken with the high-flow charcoal tube at site 2, the site with the highest concentration of benzene (Fig. 6a) and of a gasoline-oil mixture taken from a chainsaw (Fig. 6b). The gasoline-oil mixture was analyzed on 7/27/98, when there was a peak at 7 minutes in the solvent chromatogram and the benzene peak had moved more onto the shoulder of the solvent peak. For comparison, chromatograms for blanks and standard solutions can be found in Figure 7.

During GC-MS analysis, each substance was identified by comparison of its mass spectrum with those found in a library of spectra (Wiley 138) available on the computer used to operate the GC-MS. For most samples, the largest peaks in the chromatogram

were those corresponding to substances present in gasoline. All of the samples also included at least small amounts of substances not found in gasoline. All samples contained a substance which was identified as limonene (or possibly bornylene), in a few cases with peaks as large as or even larger than those from the substances present in gasoline. Half of the samples also contained α-pinene. Other substances found in two or more samples include large alkanes, methylcyclohexane, and 2-butoxyethanol.

Figure 7 shows chromatograms for blanks and standard solutions analyzed on two different dates. The first set of samples was analyzed on 7/7/98, and the chromatograms for blanks and standards were similar to those in figures 7a and 7b for the dates that all other samples from sites were analyzed. The solvent peak is centered at about 6 minutes, and in the blank there are no noticeable peaks after the solvent peak (Figure 7a). The benzene peak in the 80 mg/L standard solution is on the tail end of the solvent peak (Figure 7b), so that the integration of the benzene peak is not greatly affected by the presence of the solvent peak unless the benzene peak is very small.

Once the badges and charcoal tubes from all eight sites had been analyzed, the GC-FID was used to analyzed the thermal desorption tubes. After those analyses were completed, the GC-FID was used to analyze the badges that were loaded to determine efficiency as well as the solutions of gasoline. From the chromatograms of a blank and a standard, it became apparent that something had changed since the previous analyses had been carried out. The solvent showed a peak at 7 minutes that had not been present previously (Figure 7c), and the benzene peak had shifted to a slightly earlier retention time, moving it more onto the shoulder of the large solvent peak (Figure 7d). At first, I

Figure 7: Chromatograms of Blanks and Standard Solutions

Figure 7a: blank (solvent only); analyzed 7/7/98

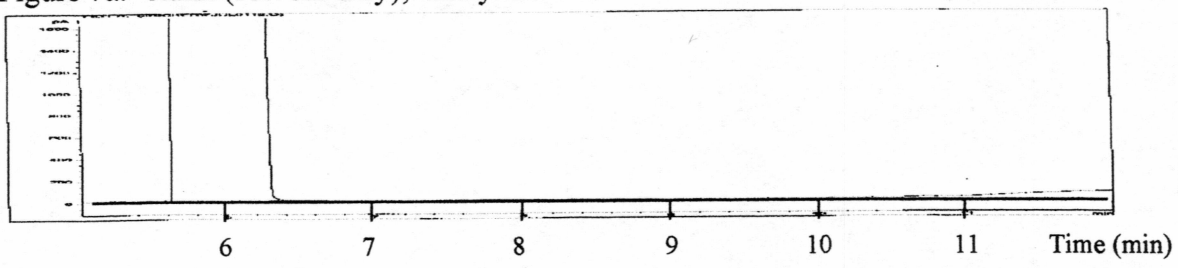

Figure 7b: 80 mg/L benzene in methylene chloride; analyzed 7/7/98

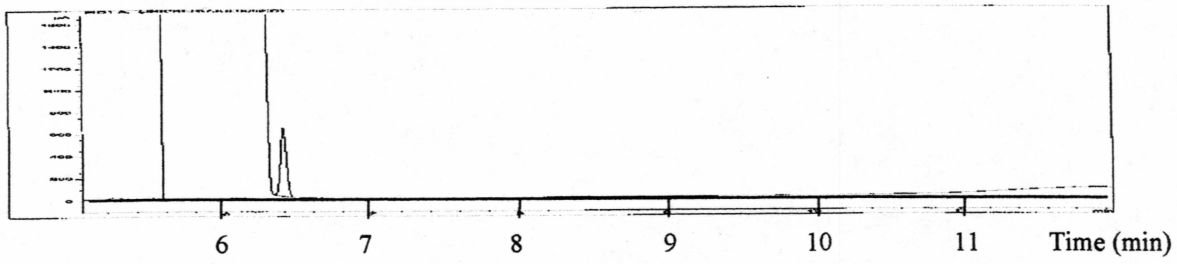

Figure 7c: blank (solvent only); analyzed 7/27/98

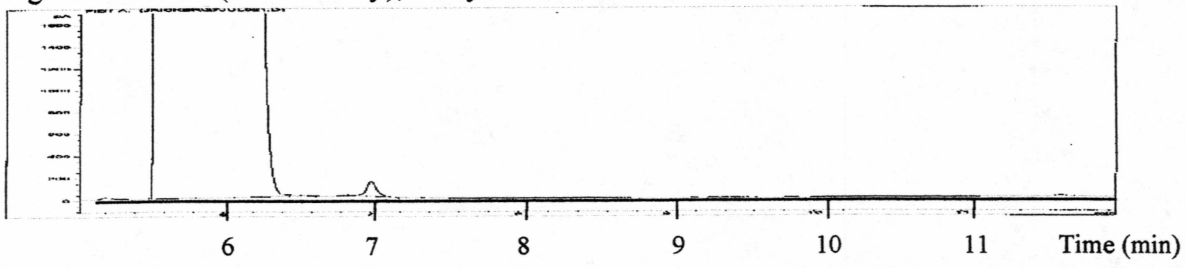

Figure 7d: 80 mg/L benzene in methylene chloride; analyzed 7/27/98

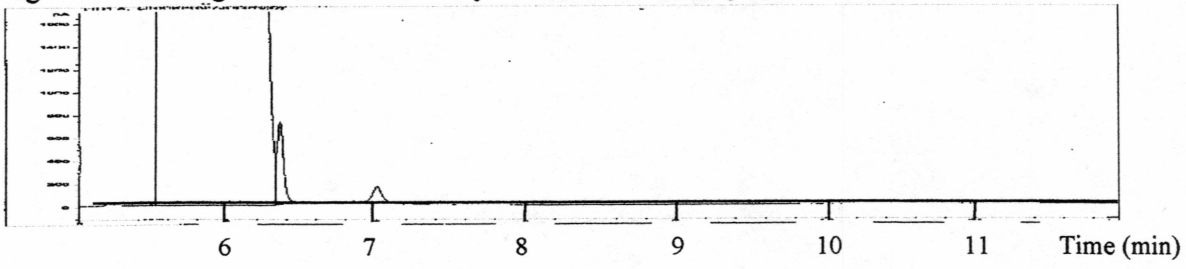

Figure 7: GC-FID chromatograms for blanks and standards analyzed on two different dates. Note that the solvent analyzed later (Fig. 7c) has an additional peak at 7 minutes that is not present in the solvent analyzed previously (Fig. 7a). The standard solution analyzed later (Fig. 7d) shows the benzene peak more on the shoulder of the solvent peak than does the standard analyzed earlier (Fig. 7b). These differences are probably due to changes in the column that occurred over time with use.

thought that the peak at 7 minutes represented some type of contaminant. Baking out the column and running solvents through the column did not remove the peak at 7 minutes, nor did replacing the septum, replacing the glass inlet liner, cleaning or replacing the syringe, or cutting off the first few inches of the column. After all of these attempts to clean the GC-FID of possible sources of contamination, the peak at 7 minutes was still present in solvent taken from a new bottle of the same brand and lot number. This suggests that the solvent I was using had not become contaminated, but that the substance producing the peak at 7 minutes had been present in the solvent all along. Apparently, the column had changed with use, resulting in these differences in the chromatograms as compared to chromatograms run earlier. The shift of the benzene peak onto the shoulder of the large solvent peak made it more difficult to integrate the benzene peak, especially since the benzene peaks were relatively small. Therefore, the badge efficiencies determined from the analysis of these chromatograms may not be accurate. However, the badge efficiency determined is probably a reasonable estimate, and will be used in calculations until permeation oven studies can be done to better determine badge efficiency.

Table 7 outlines some of the conditions at the sites sampled and includes the variables that are thought to be most likely to contribute to benzene concentrations in the home. At all sites, the garage was attached to the home. Most homes had at least one vehicle stored in the garage. At all sites, a variety of paints, stains, solvents, glues, or gasoline were also stored in the garage. An oil-burning furnace was located in most garages. At most sites, the windows of the home were closed during the sampling period.

Table 7: Site Conditions

Site	Benzene Conc.	# of Vehicles	# of Small Engines	Gas Containers	Furnace	Paints or Stains	Solvents	Glues	Windows
2	high	2	4	no	no	yes	yes	yes	closed
4	high	0	2	yes	yes	yes	yes	yes	closed
5	medium	0	1	yes	no	no	yes	yes	closed
6	medium	1	0	no	yes	yes	yes	no	closed
7	medium	1	0	no	yes	yes	yes	yes	closed
8	medium	1	0	yes	yes	yes	no	yes	open
1	low	1	0	no	yes	yes	yes	yes	open
3	low	1	0	no	yes	yes	no	no	closed

Table 7: Conditions at each site sampled during the summer of 1998. *Benzene concentration* refers to the relative concentration of benzene in air sampled inside the home. (High $\geq$ 20 ppbv; medium $\geq$ 4 ppbv; low $\geq$ 0 ppbv.) *Windows* indicates if all windows in the home were closed during the sampling period, or if some windows were open. Other variables refer to items present in the garage during the sampling period. At all sites, the garage was attached to the home.

The two sites with the highest concentrations of benzene had several small engines (such as lawnmowers and chainsaws) stored in the garage. One of the homes with medium levels of benzene had one small engine stored in the garage, while none of the other homes had small engines in the garage. A graph of the average concentration of benzene at a site versus the number of small engines stored in the attached garage at that site is shown in Figure 8.

Figure 8: Benzene Concentrations and Small Engines

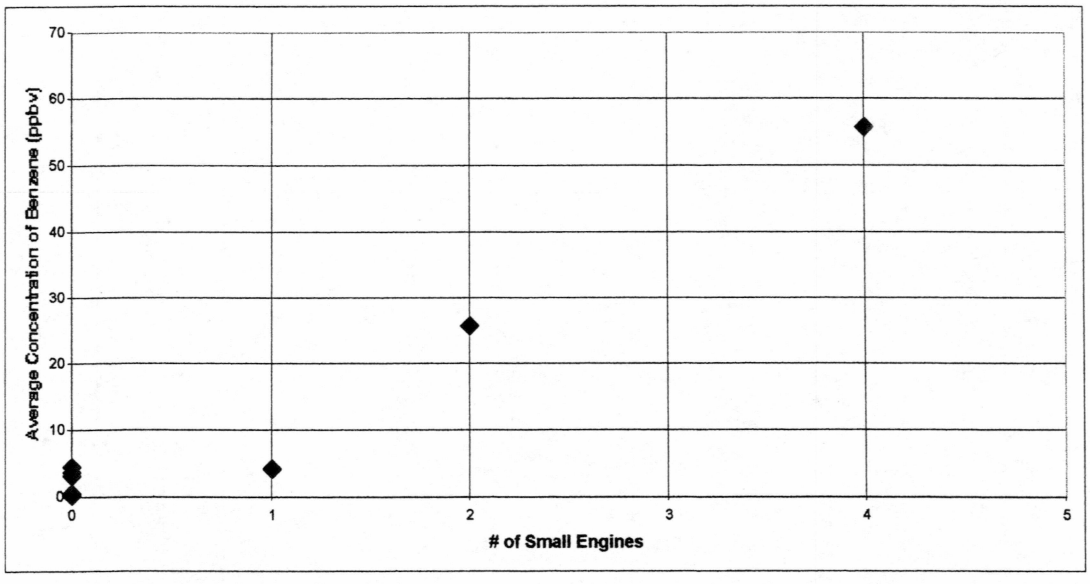

Figure 8: A graph of the average concentration of benzene at a site versus the number of small engines stored in the attached garage at that site.

Chapter 4

DISCUSSION

4.1 Comparison of Charcoal and Carbotrap Tubes

The results in Table 1 clearly show that the charcoal tubes are more efficient than the Carbotrap tubes: 60% for the charcoal tubes versus 12% for the Carbotrap tubes. The presence of benzene in the breakthrough portion of the Carbotrap tubes suggests that the efficiency is low for those tubes because much of the benzene is passing through the tube instead of being adsorbed. This may be due to the sampling rate used (about 1.6 SLPM), which is much higher than the maximum rate of 0.5 L/min recommended by ORBO for the Carbotrap tubes. (The maximum recommended rate for charcoal tubes is 1.0 L/min.) It is possible that the Carbotrap tubes would be more efficient with a slower sampling rate. Such a low flow rate was not practical for this study, because the concentrations of benzene we found are very low, requiring a large volume of air to be sampled. Therefore, charcoal tubes were used for the remainder of this study. Low sampling flow rates might be possible even for low concentrations of benzene if the sampling time was greatly increased.

4.2 Comparison of Sonication Times

The results in Table 2 suggest that there may be a slightly higher efficiency with a 4-hour sonication time than with a 30-minute sonication time. However, this difference in efficiency could be explained by the small but noticeable loss of liquid that was observed for the 4-hour sonication time. Since the difference in efficiency is not very great and a loss of liquid during sonication probably depends on the quality of the seal and is not desirable, a 30-minute sonication time was used for all subsequent analyses.

4.3 Effect of Sampling Time and Concentration of Benzene on Efficiency

The results in Table 3 and Figure 3 suggest that efficiency does not vary significantly for different concentrations of benzene sampled for different amounts of time. This means that efficiency can be determined based upon any reasonable sampling time and concentration of benzene, and the efficiency should be valid for all samples collected under a variety of conditions.

A second extraction recovered additional benzene from the charcoal, about 30-40% of the mass recovered in the first extraction. Some of this additional benzene found in the second extraction could be benzene that was dissolved in the small amount of liquid that remained in the charcoal after the first extraction, but this probably does not explain the entire amount of benzene recovered in the second extraction. This suggests that additional extractions would increase the overall efficiency of the method. Performing a series of extractions could possibly decrease the variation in efficiency between samples, as well. It is expected that the relative amount of benzene remaining in

the charcoal would vary significantly after the first extraction, especially since the extraction efficiency is less than 100%, but would vary less with successive extractions. For these reasons, a series of three extractions was performed when analyzing samples collected during the summer of 1998, with the liquid from all three extractions being added to the same autosampler vial for GC-FID analysis.

All tubes performed similarly except for one tube which had benzene in the breakthrough bed. According to Lodge (1989), the breakthrough capacity of the main bed is 6 mg for benzene. This capacity clearly has not been exceeded in this case, since only 102.3 μg (0.1 mg) of benzene was recovered from the main bed of this tube. If other organic compounds were also present in the air, they could displace benzene from the charcoal (Lodge, 1989). This could occur during actual sampling of homes, when many organic compounds could be present. However, when tubes are loaded from the permeation oven, benzene should be the only organic compound present in significant amounts. The efficiency calculated for this tube should be valid as long as the benzene found in the breakthrough bed is included in the calculation, since the amount of benzene in the breakthrough bed is less that 25% of that found on the main bed. However, the presence of benzene in the breakthrough bed does suggest a problem with the data from this tube, especially since the capacity of the main bed was not exceeded. It is possible that the charcoal in the main bed shifted in such a way as to open up channels that allowed air to pass through the main bed relatively quickly without all of the benzene being adsorbed by the charcoal in the main bed. The benzene that passed through the main bed could then have been adsorbed by the charcoal in the breakthrough bed. The

efficiency for this tube lies within the range of efficiencies determined for other tubes, so it is not likely that a significant amount of benzene passed through both beds of this tube without being adsorbed.

4.4 Permeation Rate

There was quite a bit of variation in the permeation rate during the standardization and method development phase of this project (Figure 4). If the conditions in the permeation oven remain constant, one would expect the permeation rate to be constant. The change in slope between series could be explained by the lack of gas flow through the permeation oven for the period of time between series. While no air was flowing through the oven, the rate of diffusion of benzene from the permeation tube would decrease as the concentration of benzene in the permeation oven chamber increased. However, one would expect the slope of the line representing each series to be the same, if conditions in the oven were the same for periods of time during which air was flowing through the oven. This would be the case if the conditions in the permeation oven reached equilibrium fairly quickly once gas flow was restored. If a longer period of time is required for the conditions to reach equilibrium, then one might expect the permeation rate to be larger when gas flow is first restored, then decrease over time until a steady permeation rate is reached. If it takes several days to a week for equilibration to occur, this could explain the differences in permeation rate observed in Figure 4, since permeation rates are highest after long interruptions of gas flow. In future permeation oven studies, care should be taken to prevent the interruption of gas flow, and the oven

should be allowed to equilibrate for 1-2 weeks before beginning measurements. It should be determined that the permeation rate has been constant for a period of at least 2-3 weeks before any tubes or badges are loaded from the permeation oven.

It is possible that the temperature of the oven varied slightly. Oven temperature was monitored during the last week of use (8/6-12/97), and the temperature only varied by $\pm$ 0.1 $^{\circ}$C. However, the temperature was a few tenths of a degree above the highest mark on the thermometer, so it is possible that the thermometer could not accurately read higher temperatures. The permeation oven was set up again for two months in the fall of 1997, with the temperature set a few degrees lower so that the temperature would remain within the range of the thermometer on the oven, and the temperature variations remained within $\pm$ 0.1 $^{\circ}$C. It is not likely that the oven temperature varied significantly, as the oven is designed to carefully control the temperature.

Near the end of the initial work on the project, I realized that there were air currents in the lab that were affecting the balance used to mass the permeation tube, which could explain some of the scattered data points. Also, the balance had not been re-calibrated recently, which could explain the scatter and the different slopes if the calibration of the balance was changing with time. Since then, a box was placed around the balance to minimize air currents around it, and the balance has been calibrated before each use. These practices should continue during future studies.

As previously discussed, the permeation rate used affects the efficiency measurement that is determined. Also, the method of analysis used during the sampling of homes is different from that used during the method development phase of the project,

in that there were multiple extractions of each sample. For these reasons, permeation oven studies should be repeated to better determine the efficiency of the multiple extraction method.

4.5 Determination of Extraction Efficiency for Badges

As shown in Table 5, an efficiency of 32% was determined for badges by loading a solution of benzene in hexane directly onto the badges. The efficiency determined by 3M scientists using a similar method is 97% (3M Company, 1996). One would expect the two efficiencies to be more similar. However, the 3M efficiency was determined by loading larger amounts of liquid benzene onto the badges, instead of a solution of benzene in hexane, because the badges are typically used to measure occupational exposures in situations that involve much higher concentrations of benzene (greater than 1 ppmv). Also, in processing the badges, 3M uses a single 1.5 mL extraction with carbon disulfide as the solvent (3M Company, Technical Data Bulletin No. 59; 3M Company, 1997). The method used to determine badge efficiency for this study involved a single 1 mL extraction with methylene chloride as the solvent.

Although the 32% efficiency is most likely a reasonable estimate, it may be different from the actual efficiency of the overall sampling and analysis. When sampling occurs, benzene from the air diffuses through the white film covering the badge and is then adsorbed by the charcoal pad inside the badge. This method of determining efficiency loads a liquid solution containing benzene onto a filter that is sealed inside the badge, and benzene then diffuses from the filter and is adsorbed onto the charcoal pad. It

is assumed that all of the benzene loaded onto the filter is adsorbed by the badge, but this may not be the case. This 3M method does not represent actual sampling conditions as well as would a method that exposes the badge to air containing a known concentration of benzene. Also, calculations used to determine efficiency rely on 3M's determination of a sampling rate for benzene. Determining efficiency using the permeation oven, as previously described for charcoal tubes, would probably provide a more reliable measure of the overall efficiency of the method. Once a permeation oven is available, such studies can be performed.

There is another factor that suggests this estimate of efficiency may not be reliable. The amount of benzene to load onto each badge was determined so that a peak of reasonable size would be produced on the GC-FID chromatogram, yet be representative of the amount of benzene we expect to be adsorbed during sampling. This amount was equivalent to that which would be adsorbed by a badge used to sample for 5 days in concentrations of benzene similar to those found at sites with the highest concentrations of benzene in the summer of 1998. A 5-day sampling time was chosen because it was clear from this summer's results that the badges would only be useful if sampling times were extended to at least 5-7 days, to produce large enough peaks on the chromatograms for reliable analysis. However, column performance had changed by the time samples from the loaded badges were analyzed, so that the benzene peak had moved more onto the shoulder of the solvent peak (Figure 7). This made it more difficult to integrate the peaks, since they were very small peaks on the shoulder of the very large solvent peak. For this reason, efficiencies determined from these analyses have a higher

degree of uncertainty and need repeating. Before permeation oven studies are conducted to determine the efficiency of badges, GC-FID conditions should be modified to maximize separation of the benzene peak from the solvent peak. The amount of benzene loaded could also be increased, although this would represent a longer sampling period or higher concentrations of benzene in the air being sampled. Sampling times should then be adjusted accordingly.

4.6 Sampling of Homes

A wide range of benzene concentrations, about 0-70 ppbv, was observed at the eight sites sampled during the summer of 1998 (Figure 5). These values are similar to those observed in homes in Valdez, Alaska during the summer and winter (Goldstein et al, 1992), as well as those observed indoors in non-garage locations in Fairbanks during the winter of 1992-1993 (Gordian and Guay, 1995).

The highest concentration observed, about 70 ppbv, approaches the NIOSH and ACGIH limits for workplace environments, 100 ppbv averaged over the normal workday. Most of the homes sampled had concentrations of benzene at or above the 4 ppb level. This level has been estimated by the EPA to result in one additional case of leukemia per 10,000 people exposed (Gordian and Guay, 1995). It is possible that benzene concentrations would be greater during the winter than they are during the summer, as observed in Valdez (Goldstein et al, 1992). This suggests that there are some homes in Fairbanks with high enough levels of benzene to be of concern.

Similarities between the chromatograms of indoor air samples and those of gasoline solutions (Figure 6) suggest that the primary source of benzene in the air is most likely gasoline. Figure 8 suggests that there is a relationship between the number of small engines stored in an attached garage and the concentration of benzene found in the home. Since other variables were similar for most homes, this suggests that small engines are most likely the primary source of gasoline vapors. It is not surprising that small engines would contribute more gasoline vapors to air than would vehicles, since the gas tanks of vehicles are typically more tightly sealed than are those of small engines. (Regulations require the gas tanks of newer vehicles to be tightly sealed.) It is difficult to draw strong conclusions based on such a small number of homes sampled, but the presence of small engines in the garage points to an interesting variable to be studied in the future. Sampling a larger number of homes, during the winter as well as the summer, could help identify variables that contribute most to high benzene concentrations. This information could be helpful to people who wish to make changes to their home environment in order to minimize their exposure to benzene. If it is determined that small engines stored in an attached garage contribute the majority of benzene to the air in homes, it would be a relatively simple matter to reduce indoor benzene concentrations by storing such items outdoors in a shed or under a tarp, while still using the garage for vehicle storage.

GC-MS analyses show that there are some substances present in samples that are not found in gasoline—most commonly limonene and α-pinene. Both substances are produced by trees, such as spruce and balsam poplar (also known locally as cottonwood),

and can be found in some household cleaning and deodorizing products. In future studies, it would be helpful to note the weather (rainy or dry) during the sampling period and the type of vegetation (especially trees & shrubs) at each site, as these factors could contribute to the substances collected during sampling. The presence of substances not found in gasoline suggests that there may be other sources of benzene in addition to gasoline. To better determine the source of benzene found in homes, one could sample air outdoors and in the garage (if there is a garage attached to the home) at each site, in addition to sampling in the home. This would also allow one to compare the levels of benzene in the home to those in the garage. For people who spend a significant amount of time working in their garage, this would especially be of interest.

The benzene concentrations as determined by different methods at the same site differ somewhat. There are several possible explanations for these differences. The benzene concentrations as determined using charcoal tubes could be lower than actual concentrations, since a 100% efficiency was assumed during calculations, while the actual efficiency is probably something less than 100%. The benzene concentrations as determined using badges may not be accurate for two reasons. The benzene peaks on the chromatograms were very small, making it difficult to integrate them accurately. Using badges to sample for longer periods of time (at least 5-7 days) would probably eliminate this problem. Also, the efficiency of 32% used in calculations may not be accurate, as previously discussed. Permeation oven studies to better determine efficiencies for both charcoal tubes and badges would eliminate this possible source of error.

It is not clear why there are differences between the concentrations of benzene as determined by two tubes of the same type with different flow rates. One would expect these to be the same, since the two tubes simply sampled different volumes air at the same location during the same period of time. It is possible that this much variation would be seen between samples that were taken at the same flow rate. In the future, studies should be done to determine the precision and detection limit of the method by taking multiple samples at the same site at the same time, using the same flow rates. This would allow one to determine whether or not two concentrations are significantly different, as well as the minimum concentration that could be detected. If the variation between replicate samples is not enough to explain the differences between measurements taken at different flow rates, a permeation oven could be used to perform a study to determine if the sampling flow rate affects efficiency. If so, the appropriate efficiency could be determined and used for samples collected at a given flow rate.

In spite of the differences in benzene concentrations determined by different methods, all three methods agree as to the relative benzene concentration (high, medium, or low) at each site as compared to other sites sampled, except for the problems associated with using the badges for low to medium concentrations. For the purposes of identifying the relative amount of exposure to benzene experienced by someone living in the home, any of these three methods could be used, although there were some problems associated with the badges. The amount of benzene adsorbed by the badges during an 11-12 hour sampling period was too small to be reliably measured. However, the badges could be used for a longer sampling period of at least one week, which would be

reasonable given that exposure to benzene in home environments would typically be over long periods of time.

4.7 Preferred Sampling Method for Future Studies

From this comparison of sampling methods, it is not clear which method would be best to use for future studies of benzene in air. Each method has advantages and disadvantages, and all three methods produce similar results.

The badges are the simplest device to use for sampling, since no pump or other apparatus is required—the badge is simply opened and clipped in any handy location. The badge is small enough that it is not obtrusive, and use of the badge eliminates the noisy pumps required by active sampling methods. Although the badges themselves are relatively expensive (nearly $20 each), they do not require other expensive equipment such as pumps, so they would be the preferred method if one wanted to sample many locations at the same time. This would be desirable if one wanted to sample a large number of homes in a relatively short period of time. The badges are simple enough to use that one could easily train a group of students working on a school-related project, or homeowners themselves, to set them up, eliminating the need for the researcher to visit each site. This would make it more realistic to sample a large number of homes in a short period of time.

The charcoal tubes are much less expensive than badges (less than $1 each), and the thermal desorption tubes are more expensive (about $40 each) but can be re-used once analysis is complete. Thermal desorption tubes could be cost effective if a

relatively small number of sites were sampled, then analysis of those samples could be completed before additional sites were sampled. However, they would not be cost effective if a large number of sites needed to be sampled before analysis could be completed. Use of thermal desorption tubes eliminates the problem of solvent interference that is sometimes encountered during GC-FID analysis of the charcoal tube and badge samples.

Both types of tubes require a pump, so they would only be cost effective if one sampled only a few locations at the same time. This means that it would take a long period of time to sample a large number of homes. Also, the sampling apparatus used with tubes is a bit more obtrusive than are badges. The pump is noisy, although more expensive pumps are available that are very quiet, and the apparatus takes up much more space than a badge and must be guarded against intrusion by children and pets. The charcoal tube apparatus also takes a bit more time to set up than do badges. The glass tubes must be cut open, flow rates must be adjusted once the tubes are in place, and rotameters and vacuum gauges must be read at the beginning and end of the sampling period. The thermal desorption tubes are a bit easier to set up than the charcoal tubes, since they do not need to be cut open, and the low flow rates used do not create a pressure drop across the tube so vacuum gauges are not part of the apparatus. The pump used with the thermal desorption tubes in this study could also be used to set and maintain flow rates, eliminating the need for needle valves and rotameters. Such a pump, although more expensive than the type used with charcoal tubes for this study, could probably also

be used with the charcoal tubes, as long as the total flow rate through the two charcoal tubes was within the capability of the pump.

Chapter 5

CONCLUSION

The method development work carried out with adsorbent tubes showed that, for sampling flow rates of about 1.6 SLPM, the efficiency of the method is much greater for charcoal tubes than for Carbotrap tubes. It was also shown that a sonication time of 30 minutes was adequate, since efficiencies were not much greater when a 4-hour sonication time was used. Efficiency did not vary noticeably for air with different concentrations of benzene or for air sampled for different periods of time, so an efficiency determined based upon any reasonable sampling time and concentration of benzene should be valid for all samples collected under a variety of conditions. A second extraction recovered additional benzene, suggesting that a method involving multiple extractions would result in a greater efficiency than one that uses only one extraction. Based upon these results, the method used to sample the air in homes used charcoal tubes which were processed with three solvent extractions and a 30-minute sonication time.

Problems related to the determination of efficiencies for charcoal tubes and badges suggest that permeation oven studies should be performed in order to better determine these efficiencies. Before efficiency studies are begun, a careful determination of permeation rate should be carried out, with conditions controlled so that the permeation rate remains as constant as possible during the study period. It may be wise to determine the efficiency for each of the sampling flow rates used.

Sampling of a limited number of homes during the summer of 1998 found a range of benzene concentrations as high as about 70 ppbv, which approaches the NIOSH and ACGIH limits for workplace environments of 100 ppb over an 8-10 hour workday. The concentration in most homes was at or above the 4 ppb level estimated by the EPA to result in additional cases of leukemia. Since concentrations may be higher in the winter than they are in the summer, sampling of a larger number of homes during the winter should provide valuable new data. This could also provide a better measure of typical benzene concentrations found in homes in Fairbanks, where winter lasts for nine months of the year.

Results of this preliminary study suggest that the primary source of benzene in the homes sampled was gasoline, most likely from small engines stored in an attached garage. Sampling a larger number of homes, including a variety of homes which differ in variables that are expected to contribute to benzene concentrations, could help identify other factors that contribute most to high benzene concentrations. Variables of interest include attached garages, ventilation systems, type of heat (wood, oil, etc.), and the presence of smokers in the home. This would provide useful information to people who wish to make changes to their home environment in order to minimize their exposure to benzene.

Two of the methods used for sampling during this project—charcoal tubes and thermal desorption tubes—would be appropriate to use for future studies of benzene in air. Before passive-sampling badges are used in future studies, they should first be tested with longer sampling times to determine whether or not they are appropriate for use with

low concentrations of benzene. The choice of method would depend on a variety of factors, including the amount of funding available as well as the sampling design. Factors related to sampling design include the number of sites being sampled at the same time, whether analyses were to be completed between small sets of samples or after a large number of samples had been collected, and the desire to make the sampling technique unobtrusive. Who is doing the sampling—a small number of trained researchers or a large group of people with little training, such as students or homeowners—may also influence the choice of method.

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